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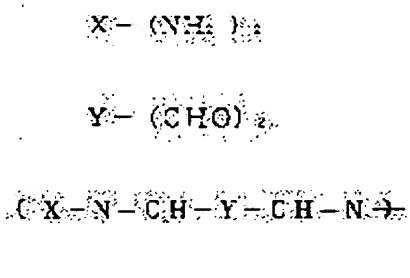
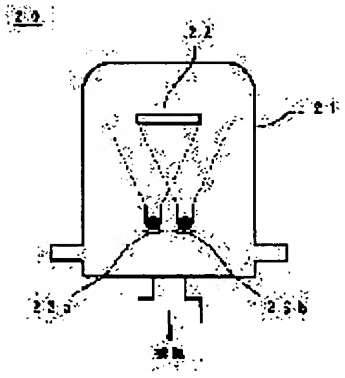
(54) POLYAZOMETHINE, ITS PRODUCTION AND THIN FILM ELECTROLUMINESCENT ELEMENT

(57)Abstract:

PURPOSE: To obtain a polyazomethine improved in the ability to transport electrons, the ability to emit electroluminescence, the ability to transport holes, heat resistacne and durability by reacting a specified diamino compound with a specified dialdehyde compound.

CONSTITUTION: A substrate 22 is set within the vacuum deposition chamber 21 of a vacuum deposition apparatus 20, a diamino compound of formula I (wherein X is an aromatic hydrocarbon group or a group derived from a heterocyclic compound) and a dialdehyde compound of formula II (wherein Y is a group having an aromatic tert. amine skeleton), both of which are used as polymerizable monomers, are placed in their respective vapor deposition sources 23a and 23b. The chamber 21 is evacuated until the inside pressure decreases to 10-2 Pa or below, while the temperature of the deposition surface of the substrate 22 is adjusted to -50 to 200°C. After the pressure inside the chamber 21 reaches a specified value, the temperatures of the vapor deposition sources 23a and 23b are adjusted to -10 to 500°C so that the monomers may be vaporized in a molar ratio of the diamino compound to the dialdehyde compound of 1:(1-30), and that the deposition film may be formed at a rate of deposition of 0.1-10Å/sec. Thus, a deposition





film of a polyazomethine of formula II is formed on the substrate 22.

LEGAL STATUS

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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the thin film electroluminescence devices used in more detail as the polyazo methine used as a thin film electroluminescence ingredient etc., its manufacture approach and a flat-panel display, or its back light about the thin film electroluminescence devices which have the layer which consists of new polyazo methine, its manufacture approach, and this polyazo methine.
[0002]
[Background of the Invention] Since organic thin film electroluminescence devices are perfect solid-state components, they are excellent in shock resistance, and it has the description that visibility is high, for self-luminescence, and research used as a current flat panel mold display is done actively.
[0003] Organic thin film electroluminescence devices are components which emit light in the light (fluorescence) of an ingredient proper, when the hole and electron which were poured in by impressing an electrical potential difference from an electrode to a specific organic material recombine and ease within the ingredient. As an organic material used for such a component, the anthracene single crystal which carries out electroluminescence blue is known for many years. However, since this single crystal has thickness as thick as dozens of micrometers - several mm, in order to make it emit light, the driver voltage of hundreds V was required for it. Then, although driver voltage was reduction-ized by thin-film-izing, injection efficiency is not yet enough.
[0004] Moreover, the laminating mold electroluminescence devices using an organic material are also reported, these laminating mold electroluminescence devices carry out the vacuum evaporationo laminating of a hole impregnation layer, a luminous layer, and the electronic notes telegram pole of Mg:Ag to this order on ITO, and luminescence is observed with the applied voltage of dozens V. However, a component may stop having emitted light and between the layers which the vapor-deposited ingredient crystallizes and consist of an electrode and an organic material by generation of heat accompanying luminescence might exfoliate.
[0005] The attempt which macromolecule-izes an organic material occurs as a means to solve such a problem, a low molecular weight compound is added or the electroluminescence devices which used pi conjugated-system polymeric materials for charge transportability polymeric materials are reported. For example, the minute amount dope of the luminescent coloring matter is carried out, it considers as a spin coat thin film in Pori (methylphenyl silane) known as a hole transport ingredient, and the two-layer laminating mold electroluminescence devices which carried out vacuum deposition of the electronic transport ingredient, and produced it to this, the monolayer mold electroluminescence devices which added and carried out the spin coat of luminescent coloring matter and the electronic transportability compound to Pori (N-vinylcarbazole) which is a hole transport ingredient, and produced them to it are proposed. On the other hand, the macromolecule electroluminescence devices using Pori (phenylenevinylene) which is pi conjugated-system polymeric materials and the copolymer and a partial conversion object, Pori (p-phenylene), Pori (alkyl thiophene), and Pori (full I non) are also reported. It is

expected by using these polymeric materials that crystallization of the thin film by generation of heat which poses an endurance top problem of electroluminescence devices is substantially improvable.
[0006] However, when the wet process which forms a thin film from a solution as a production process of a macromolecule thin film is adopted, various impurities may be made to mix into a component, or a front face may be polluted.
[0007] Moreover, in case spreading formation of the organic layer is further carried out on the once formed organic thin film, the solvent used in case spreading formation of the upper layer is carried out must choose that in which a lower layer is not dissolved or eluted, and the applicability of selection of polymeric materials or the low-molecular ingredient made to contain is restricted.
[0008] Then, the vacuum evaporationo polymerization method which is a method of producing the electroluminescence devices by the dry process is proposed. The production approach of the electroluminescence devices by the vacuum evaporationo polymerization method is indicated by JP,5-271651,A. However, since the smoothness of tetracyano quinodimethan (TCNQ), tetra-thio full BAREN (TTF), etc. which are the molecule which bears charge transport to show an electroluminescence function etc. is high, they are in a lifting or a cone inclination about crystallization. Moreover, in Pori (N-vinylcarbazole) which has a charge transport radical in a side chain, since the smoothness of these molecules is high, an intermolecular interaction is caused and dimerized, it is reported that the dimer part serves as a trap of charge (hole) transport, and the disadvantageous field for charge transport exists with the macromolecule thin film which has a charge transport radical in a side chain.
[0009] Therefore, it is possible that the radical which bears ** charge transport in which ** smoothness has collapsed exists in the principal chain of a macromolecule as conditions required of the molecule which bears charge transport etc. It is expected by fulfilling these conditions that highly efficient organic thin film electroluminescence devices become possible.
[0010]
[Objects of the Invention] This invention is made in view of the above actual condition, and it aims at offering thin film electroluminescence devices excellent in thermal resistance and endurance while it aims at offering the polyazo methine suitably used as a thin film electroluminescence ingredient, and its manufacture approach.
[0011]
[Summary of the Invention] The polyazo methine concerning this invention is characterized by having the repeat unit expressed with the following type [I].
[0012]
[Formula 3]

$$\text{-}\left(\text{X}-\text{N}=\text{CH}-\text{Y}-\text{CH}=\text{N}\right)\text{-} \quad \cdots \quad [\text{I}]$$

[0013] (X shows among a formula the radical guided from an aromatic hydrocarbon radical or a heterocycle compound, and Y shows the radical which has the third class amine frame of aromatic series.)
Especially the polyazo methine that is the radical to which X is guided in said formula [I] from an aromatic hydrocarbon radical or four or more carbon atomic numbers nitrogen content aromatic series heterocycle compound is useful as a thin film electric-field component ingredient.
[0014] The manufacture approach of the polyazo methine concerning this invention is characterized by obtaining the polyazo methine which has the repeat unit expressed with the ****** type [I] to which the diamino compound expressed with the following type [II] and the dialdehyde compound expressed with the following type [III] are made to react.
[0015]
X-(NH2) 2 -- [II]
(X shows among a formula the radical guided from an aromatic hydrocarbon radical or a heterocycle compound.)
Y-(CHO) 2 -- [III]
(Y shows among a formula the radical which has the third class amine frame of aromatic series.)

The thin film electroluminescence devices concerning this invention have an electroluminescence layer in inter-electrode [of a couple at least with transparent one side]. And while having hole impregnation and a transporting bed, or electron injection and a transporting bed between one side of said electrode, and said electroluminescence layer if needed or having hole impregnation and a transporting bed between one side of said electrode, and said electroluminescence layer In the thin film electroluminescence devices which have electron injection and a transporting bed between another side of said electrode, and said electroluminescence layer, it is characterized by at least one layer consisting of the above-mentioned polyazo methine among said electroluminescence layer, hole impregnation and a transporting bed, and electron injection and a transporting bed.

[0016] It is desirable that it is the layer obtained by said electroluminescence layer carrying out the vacuum evaporationo polymerization of the diamino compound expressed with said formula [II] and the dialdehyde compound expressed with said formula [III] in this invention.

[0017] It is desirable that it is the layer obtained by the layer which consists of said polyazo methine carrying out the vacuum evaporationo polymerization of the diamino compound expressed with said formula [II] and the dialdehyde compound expressed with said formula [III] in this invention.

[0018]

[Detailed Description of the Invention] Hereafter, the polyazo methine concerning this invention, its manufacture approach, and thin film electroluminescence devices are explained concretely.

[0019] The polyazo methine of this invention is a high molecular compound which has the repeat unit expressed with the following type [I].

[0020]

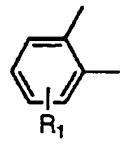
[Formula 4]

$$\text{-}\left(\text{X}-\text{N}=\text{CH}-\text{Y}-\text{CH}=\text{N}\right)\text{-} \quad \cdots \quad [\text{I}]$$

[0021] Among a formula, X shows the radical guided from an aromatic hydrocarbon radical or a heterocycle compound, and, specifically, the following radicals are mentioned.

[0022]

[Formula 5]



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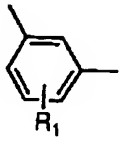

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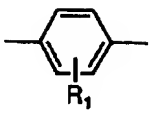

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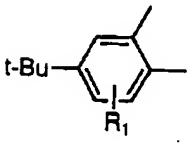

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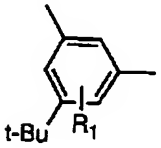

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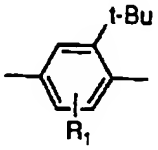

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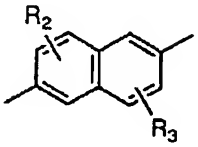

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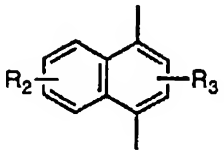

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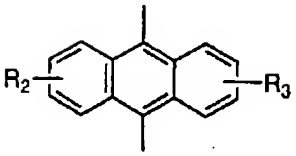

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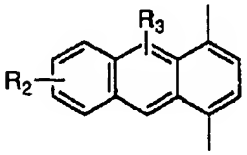

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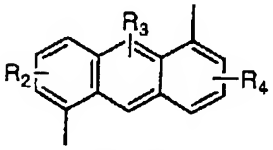

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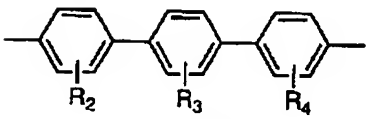

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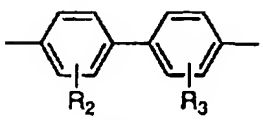

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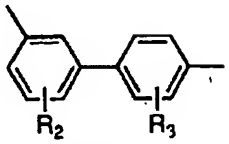

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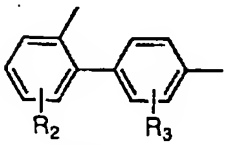

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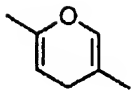

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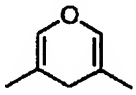

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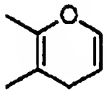

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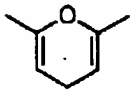

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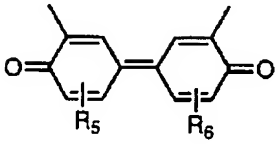

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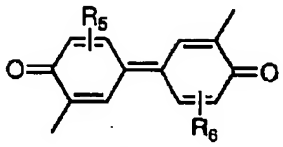

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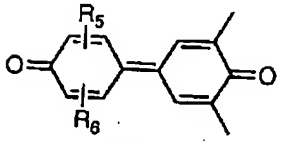

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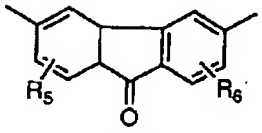

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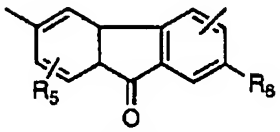
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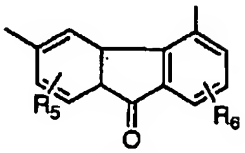
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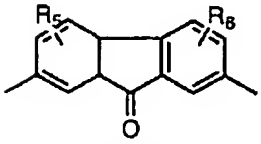
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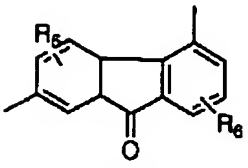
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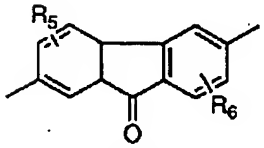
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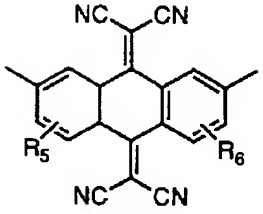
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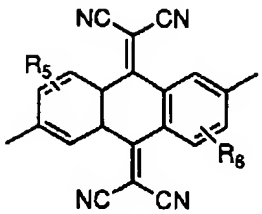
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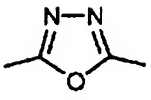
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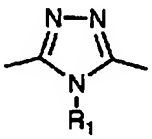
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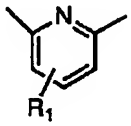
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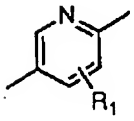
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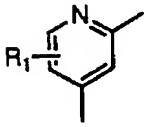
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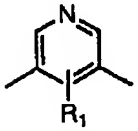
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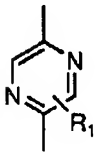
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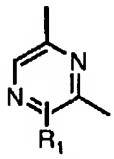
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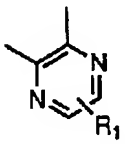
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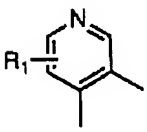
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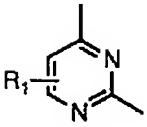
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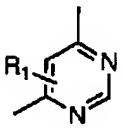
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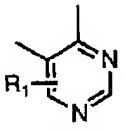
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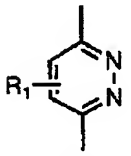
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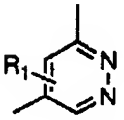
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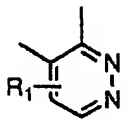
[0026]
[Formula 9]



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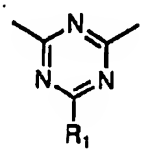

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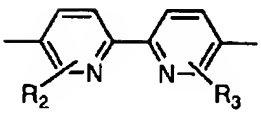

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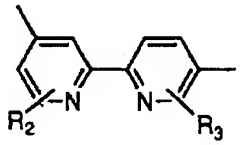

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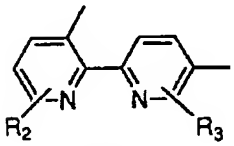

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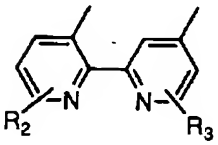

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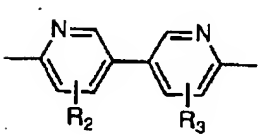

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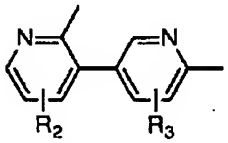

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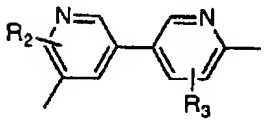

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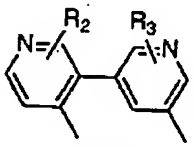
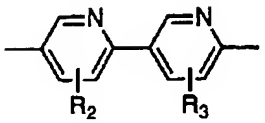


[X-55]

[0027]
[Formula 10]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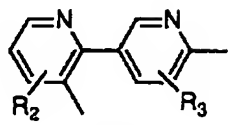
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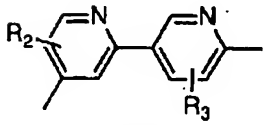
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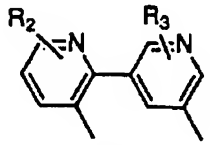
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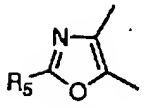
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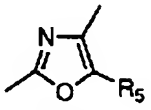
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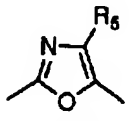
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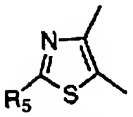
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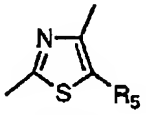
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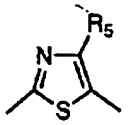
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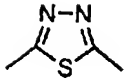
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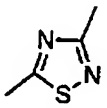
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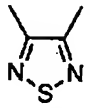
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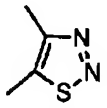
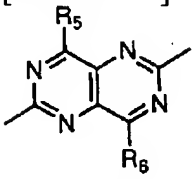
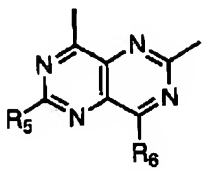
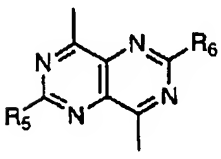

[X-69]

[0028]
[Formula 11]

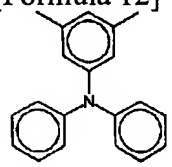

[X-70]

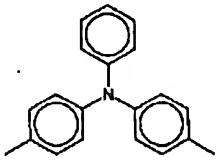

[X-71]


[X-72]

[0029] In addition, it is R1 -R6 among the above-mentioned formula. The alkyloxy radical of the carbon atomic numbers 1-10, such as carbon atomic number [, such as an alkyl group of the carbon atomic numbers 1-10, such as a hydrogen atom, methyl, ethyl, propyl, and butyl, benzyl, and phenethyl,] 7 - 10

aralkyl radical, methoxy, and ethoxy ** propoxy and butoxy one, is shown independently, respectively.
[0030] In the radical shown by the above-mentioned X, the radical guided from an aromatic hydrocarbon radical or four or more carbon atomic numbers aromatic series heterocycle compound is desirable, and the radical guided from a four or more carbon atomic numbers nitrogen content aromatic series heterocycle compound is more desirable.
[0031] Since the electronegativity of a nitrogen atom is larger than the electronegativity of a carbon atom, electronic receptiveness required for electronic transport can be raised. Therefore, electron injection and transportability can be given by using the radical guided from a nitrogen content heterocycle compound as X in a formula [I].
[0032] The radical guided from the compound currently indicated by the third class amine of aromatic series which is indicated by the derivative residue of various compounds by which Y is known for the electrophotography photo conductor etc., for example, JP,63-295695,A, or a porphyrin compound, JP,53-27033,A, JP,54-58445,A, JP,54-149634,A, JP,54-64299,A, JP,55-144250,A, JP,56-119132,A, JP,61-295558,A, JP,61-98303,A, etc. is mentioned. Such a radical gives hole impregnation and transportability.
[0033] In this invention, as for Y, it is desirable that it is the radical which has the third class amine frame of aromatic series, and, specifically, the following radicals are mentioned.
[0034]
[Formula 12]


[Y-1]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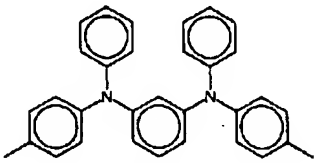
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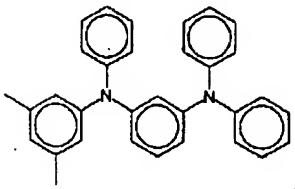
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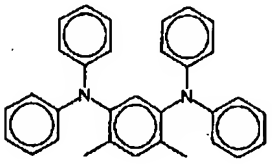
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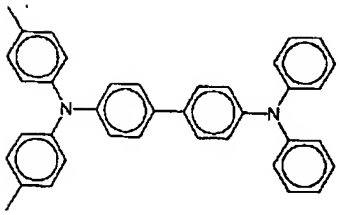
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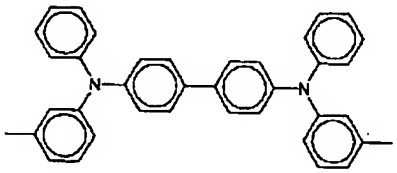
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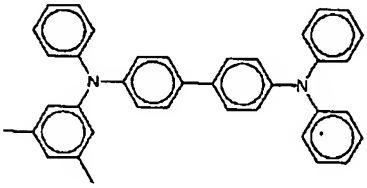
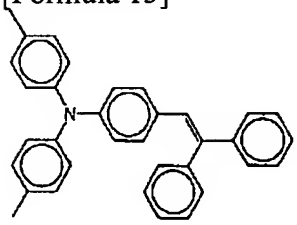

[Y-8]

[0035]

[Formula 13]



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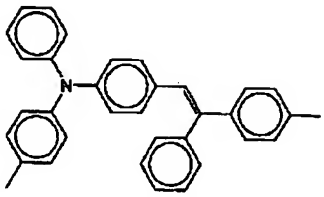
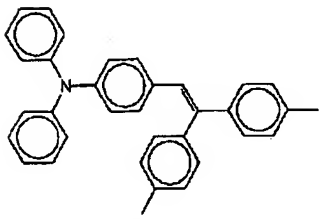
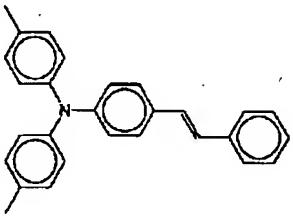


[Y-10]



[Y-11]



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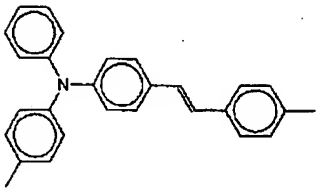

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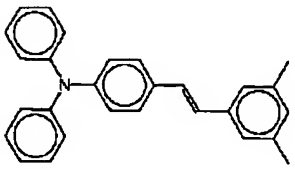

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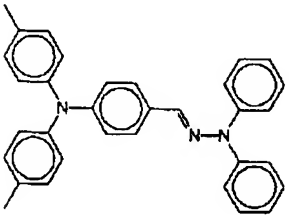

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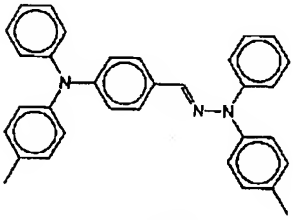
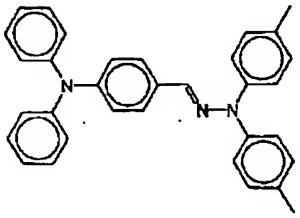
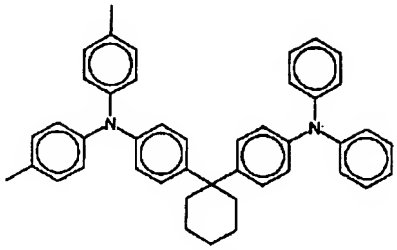


[Y-16]

[0036]
[Formula 14]



[Y-17]



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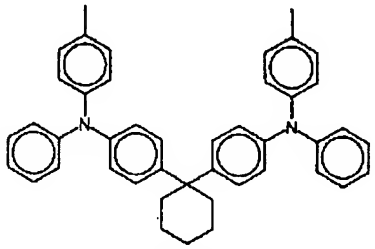
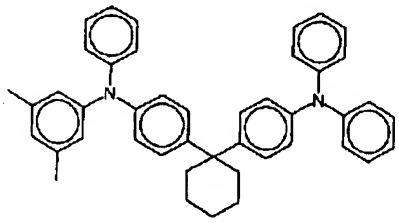
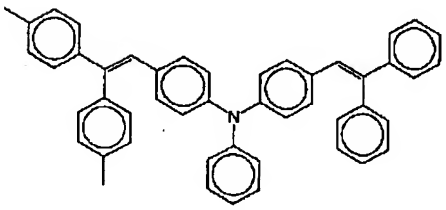


[Y-19]

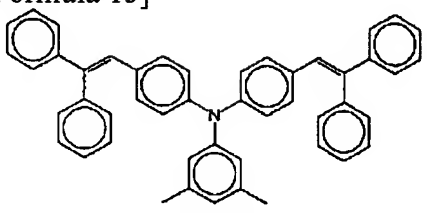


[Y-20]

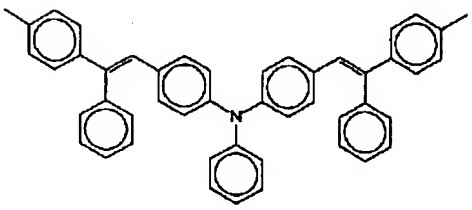


[Y-21]

[0037]
[Formula 15]



[Y-22]



[Y-23]

[0038] The radical which has the third class amine frame [like] of the above-mentioned aromatic series has the structure (pyramid mold) in which smoothness collapsed with the unpaired electron of a nitrogen atom. For a pile reason, the molecule which has the structure in which such smoothness collapsed does not become a lifting with the trap of charge transport about an intermolecular interaction, and is convenient to charge transport.
[0039] The polymerization degree of the polyazo methine concerning this invention is ten or more more preferably five or more two or more. The polymer which has the azomethine repeat unit expressed with said formula [I] can search for the polymerization degree with a viscosity method, when dissolving in polar solvents, such as dimethylformamide (DMF) and dimethyl sulfo oxide (DMSO).
[0040] The polyazo methine concerning this invention can be used as for example, a thin film electroluminescence-devices ingredient. In this case, polyazo methine can be made into an electroluminescence layer, electron injection and a transporting bed, or hole impregnation and a transporting bed by choosing suitably the radical shown by X and Y.
[0041] The radical which has an electroluminescence function and charge impregnation / transport function is included in the principal chain, it is hard to crystallize, and the polyazo methine of this invention is excellent in thermal resistance and endurance. The polyazo methine of this invention can be manufactured by making the diamino compound expressed with the following type [II], and the dialdehyde compound expressed with the following type [III] react.
[0042]
X-(NH2) 2 -- [II]
(X is the same as that of X in said formula [I] among a formula.)
Y-(CHO) 2 -- [III]
(Y is the same as that of Y in said formula [I] among a formula.)
When using the polyazo methine of this invention as a thin film electroluminescence-devices ingredient, the vacuum evaporationo polymerization of the diamino compound expressed with the above-mentioned formula [II] and the dialdehyde compound expressed with the above-mentioned formula [III] is carried out, and polyazo methine is formed as a thin film on a substrate. The method of producing the polyazo methine thin film by the vacuum evaporationo polymerization can be performed by various well-known approaches.
[0043] The diamino compound more specifically expressed with the above-mentioned formula [II] that it mentions later and the dialdehyde compound expressed with the above-mentioned formula [III] are made into the source of vacuum evaporationo, respectively, vacuum evaporationo of 2 yuan is performed within a vacuum tub, and a polyazo methine thin film is obtained by making a monomer react on a substrate.
[0044] According to such an approach, there is little mixing of an impurity, and a pinhole does not have it, either and it can form the thin film excellent in endurance. Next, the thin film electroluminescence devices concerning this invention are explained.
[0045] Drawing 1 -4 are the sectional view showing typically the configuration of the thin film electroluminescence devices concerning this invention, one in drawing shows a negative electrode, 2 shows a positive electrode, 3 shows an electroluminescence layer, 4 shows electron injection and a transporting bed, and 5 shows hole impregnation and a transporting bed. Drawing 5 is the schematic diagram showing an example of the vacuum evaporator used for manufacture of the thin film electroluminescence devices concerning this invention.
[0046] The thin film electroluminescence devices 10 concerning this invention are layered products which have the electroluminescence layer 3 between the electrodes (a negative electrode 1 and positive electrode 2) of a couple as shown in drawing 1 . As a negative electrode 1, the injection efficiency of the electron to the electroluminescence layer 3 is high, and well-known electrodes, such as the electrode which can moreover repeat and inject an electron into the electroluminescence layer 3, for example, Mg, In(s), calcium, and aluminum, and these alloys, can be used.
[0047] As a positive electrode 2, the injection efficiency of the hole (electron hole) to the electroluminescence layer 3 is high, and the electrode which carried out the laminating of Au, Pt, Ag,

etc. translucent can be used on transparent electrodes, such as well-known electrode simple substances, such as the electrode which can moreover repeat and inject a hole into the electroluminescence layer 3, for example, indium tin oxide, (ITO), tin oxide (NESA), and Au, Pt, Ag, and ITO, or NESA.

[0048] Either said negative electrode 1 and the positive electrode 2 can be transparent, and it can irradiate now the light from the electroluminescence layer 3 through this transparent electrode. Moreover, either the negative electrode 1 and the positive electrode 2 are usually formed on transparence substrates, such as glass and a polymer film. For example, the ITO electrode formed in the shape of a thin film on glass or a polymer film is used as a positive electrode 2.

[0049] The electroluminescence layer 3 is formed from the polyazo methine which has the repeat unit expressed with the following type [I].

[0050]

[Formula 16]

$$-\!\left(-X-N=CH-Y-CH=N-\right)- \quad \cdots \quad [I]$$

[0051] (X and Y are the same as that of the above among a formula.)

X and Y are suitably chosen according to the wavelength of the light which emits light from the class and the electroluminescence layer 3 of the ingredient which forms a negative electrode 1 and a positive electrode 2 etc.

[0052] The thin film electroluminescence devices 10 concerning this invention may have electron injection and a transporting bed 4 between the negative electrode 1 and the electroluminescence layer 3, as shown in drawing 2 R> 2. As shown in drawing 3 , you may have hole impregnation and a transporting bed 5 between the positive electrode 2 and the electroluminescence layer 3, and as shown in drawing 4 , it may have electron injection and a transporting bed 4 between a negative electrode 1 and the electroluminescence layer 3, and you may have hole impregnation and a transporting bed 5 between the positive electrode 2 and the electroluminescence layer 3.

[0053] Electron injection and a transporting bed 4 play the role which raises the injection efficiency of the electron injected into the electroluminescence layer 3 from a negative electrode 1, and hole impregnation and a transporting bed 5 play the role which raises the injection efficiency of the hole injected into the electroluminescence layer 3 from a positive electrode 2 here.

[0054] When the thin film electroluminescence devices 10 have electron injection and a transporting bed 4, and/or hole impregnation and a transporting bed 5, any one layer of the electroluminescence layer 3, electron injection and a transporting bed 4, and/or the hole impregnation and a transporting bed 5 is formed from the polyazo methine which has the repeat unit expressed with said formula [I]. Layers other than the layer formed from said polyazo methine are formed with the well-known ingredient.

[0055] When the thin film electroluminescence devices 10 have electron injection and a transporting bed 4, and/or hole impregnation and a transporting bed 5 in this invention, it is desirable to form the electroluminescence layers 3, electron injections and transporting beds 4, and all the hole impregnation and transporting beds 5 from said polyazo methine. In this case, the electroluminescence layer 3 is formed by polyazo methine excellent in electroluminescence nature, electron injection and a transporting bed 4 are formed by polyazo methine excellent in electron injection and transportability, and hole impregnation and a transporting bed 5 are formed by polyazo methine excellent in hole impregnation and transportability. Among X and Y in said formula [I] of the polyazo methine which forms the electroluminescence layer 3, in addition, at least one side It differs in X or Y in said formula [I] of the polyazo methine which forms hole impregnation and a transporting bed 5. Among X and Y in said formula [I] of the polyazo methine which forms the electroluminescence layer 3, at least one side It differs in X or Y in said formula [I] of the polyazo methine which forms electron injection and a transporting bed 4. At least one side differs in X or Y in said formula [I] of the polyazo methine which forms hole impregnation and a transporting bed 5 among X and Y in said formula [I] of the polyazo methine which forms electron injection and a transporting bed 4.

[0056] X and Y in said formula [I] of the polyazo methine which forms the electroluminescence layer 3 X and Y in said formula [I] of the polyazo methine which is suitably chosen according to the wavelength

of the light which emits light from the electroluminescence layer 3 etc., and forms electron injection and a transporting bed 4 According to the class of ingredient which forms a negative electrode 1 etc., it is chosen suitably, and X and Y in said formula [I] of the polyazo methine which forms hole impregnation and a transporting bed 5 are suitably chosen according to the class of ingredient which forms a positive electrode 2 etc.

[0057] The electroluminescence layer 3, electron injection and a transporting bed 4, and hole impregnation and a transporting bed 5 can be formed for example, by the vacuum evaporationo polymerization method. 100-2000A of thickness of the electroluminescence layer 3 which forms such thin film electroluminescence devices 10 is usually 200-1200A preferably, 50-2000A of thickness of electron injection and a transporting bed 4 is usually 50-500A preferably, and 50-2000A of thickness of hole impregnation and a transporting bed 5 is usually 50-500A preferably.

[0058] In this invention, you may have protective coats, such as antioxidizing film, on the negative electrode 1 of the thin film electroluminescence devices 10, or the positive electrode 2. The increase of the stability of an electrode, and the practicability and endurance as a component improve by existence of such a protective coat. A protective coat can be formed by approaches, such as a spin coat method or vacuum deposition. As such a protective coat, encapsulants, such as a metal, a metallic oxide, and a metal fluoride, can be used, for example.

[0059] The thin film electroluminescence devices of this invention are piles to a lifting about degradation by crystallization since at least one layer is formed from the polyazo methine which has the repeat unit expressed with said formula [I] among the electroluminescence layer, electron injection and a transporting bed, and hole impregnation and a transporting bed, and the exfoliation from an electrode etc. Moreover, the layer which consists of polyazo methine formed of the dry process has little mixing of an impurity, and does not have a pinhole.

[0060] Such thin film electroluminescence devices 10 of this invention can be made to emit light by impressing an electrical potential difference from a negative electrode 1 and a positive electrode 2. As for the electrical potential difference to impress, it is possible not only DC electrical potential difference but to make light emit by actuation waves, such as pulse impression and a chopping sea. when especially a pulse is used, compared with DC electrical potential difference, it is markedly alike and power consumption not only decreases, but leads to improvement in the life of a component. Thus, by driving by the wave of a specific electrical potential difference, thin film electroluminescence devices can also be used as a display device.

[0061] Moreover, the thin film electroluminescence devices of this invention can also be used as the back light which gave and drove patterns, such as a matrix electrode or a thin film transistor (TFT) electrode, as an electronic notes telegram pole and a hole impregnation electrode, and was made to unite with liquid crystal, or a display device.

[0062] Such thin film electroluminescence devices are usually manufactured through the process of following (i) - (vi).

(i) -- the process (ii) which forms the 1st electrode on a substrate -- on the electrode of the process (iii) 1st which forms the 1st charge impregnation and transporting bed by request on the 1st electrode On the process (iv) electroluminescence layer (3) which forms an electroluminescence layer (3) on the 1st charge impregnation and transporting bed when the 1st charge impregnation and transporting bed are formed at said process (ii), or by request the process which forms the 2nd the charge impregnation and transporting bed which has the capacity to pour in and convey the charge of an opposite sign with the 1st charge impregnation and transporting bed -- [-- for example, when the 1st charge impregnation and transporting bed are electron injection and a transporting bed (4), the 2nd charge impregnation and transporting bed are hole impregnation and a transporting bed (5)

(v) Process [for example, when the electrode formed at the process (i) is a negative electrode (1), a counterelectrode is a positive electrode (2)] which forms a counterelectrode on the 2nd charge impregnation and transporting bed when the 2nd charge impregnation and transporting bed are formed at an electroluminescence layer (3) top or said process (iv)

(vi) It is desirable to perform degree process, without making the open air flow in a chamber until it

results in the process which performs continuously all the processes [the process (v) from said process (i)] to the process which forms a counterelectrode on a substrate from the process which fabricates an electrode within the same chamber, and forms a counterelectrode in process this invention which forms the closure layer of electroluminescence devices on a counterelectrode by request, in case thin film electroluminescence devices are manufactured.

[0063] Thus, if thin film electroluminescence devices are manufactured, it does not adhere to the thin film which the dust contained during the open air formed, or a thin film will adsorb the oxygen or the moisture under open air, and will not deteriorate.

[0064] In the thin film electroluminescence devices of this invention, the layer which at least one layer consists of polyazo methine expressed with said formula [I] among the electroluminescence layer (3), 1st, and 2nd charge impregnation and transporting beds [electron injection, a transporting bed (4), and hole impregnation and a transporting bed (5)], and consists of this polyazo methine is formed by the vacuum evaporationo polymerization method.

[0065] In case said layer is formed by the vacuum evaporationo polymerization, the diamino compound expressed with the following type [II] and the dialdehyde compound expressed with the following formula [III] are used as a monomer for polymerizations.

[0066]

X-(NH2) 2 -- [II]

(X is the same as that of X in said formula [I] among a formula.)

Y-(CHO) 2 -- [III]

(Y is the same as that of Y in said formula [I] among a formula.)

The polyazo methine thin film which forms the thin film electroluminescence devices concerning this invention is formed as follows using vacuum evaporationo equipment 20 as shown in drawing 5 .

[0067] namely, (a) -- the vapor-deposited substrate 22 is first set in the chamber 21 for vacuum evaporationo of a vacuum evaporation system 20. (For example, when using a substrate with an ITO electrode as a vapor-deposited substrate, it sets so that the vacuum evaporationo film may be formed on an ITO electrode)

(b) Lay said monomer for polymerizations (a diamino compound [II] and dialdehyde compound [III]) in the sources 23a and 23b of vacuum evaporationo in a vacuum evaporator 20, respectively.

(c) 10 - 2 or less Pa, the pressure in the chamber 21 for vacuum evaporationo decompresses the inside of the chamber 21 for vacuum evaporationo until it becomes below 10-3Pa preferably. Moreover, by the time the inside of the chamber 21 for vacuum evaporationo reaches a predetermined pressure, -50-200 degrees C of temperature of the vapor-deposited field of the vapor-deposited substrate 22 will be preferably adjusted to 20-100 degrees C.

(d) the bottom of this pressure after the inside of the chamber 21 for vacuum evaporationo reaches a predetermined pressure -- a diamino compound [II] and a dialdehyde compound [III] -- 1:1-1:30 -- control the temperature of the sources 23a and 23b of vacuum evaporationo so that it evaporates in the mole ratio of 1:1-1:20 preferably and 0.1-10A /of vacuum evaporationo coats is preferably formed with the evaporation rate of 1-5A/second a second. -10-500 degrees C of 40-400 degrees C of 70-300 degrees C of temperature in this case are usually 100-250 degrees C especially preferably more preferably.

[0068] A vacuum evaporationo thin film is formed in desired thickness as mentioned above. When forming two or more layers which consist of polyazo methine, the monomer for polymerizations is changed and the above-mentioned process is repeated.

[0069]

[Effect of the Invention] The polyazo methine concerning this invention is used as a thin film electroluminescence-devices ingredient which forms the thin film excellent in electronic transportability, the luminescence, or hole transportability.

[0070] The thin film electroluminescence devices of this invention are excellent in thermal resistance and endurance. Such thin film electroluminescence devices can be used as a flat-panel display or its back light.

[0071]

[Example] Hereafter, although this invention is explained still more concretely based on an example, this invention is not limited to these examples.

[0072]

[Example 1]

Synthetic 5-amino isophthalic acid of 4', the 4"-dimethyl triphenylamine -3, and 5-dialdehyde, NaNO2 / KI was made to react under existence of HCl, and 5-iodine isophthalic acid was obtained. Next, it is H2 SO4 about 5-iodine isophthalic acid and ethanol. It was made to react under existence and the ethyl ester of 5-iodine isophthalic acid was obtained. Next, 4', the 4"-dimethyl triphenylamine -3, and 5-diethyl ester were obtained by carrying out the Ullman (Ullmann) reaction of this ester and the JITORIRU amine.

[0073] then, this 4' and 4" -- processing - dimethyl triphenylamine -3 and 5-diethyl ester in a sodium-hydroxide water solution -- 4' and 4" - dimethyl triphenylamine -3 and 5-dicarboxylic acid were obtained. furthermore, this 4' and 4" -- making SOCl2 - dimethyl triphenylamine -3 and 5-dicarboxylic acid react -- 4' and 4" - dimethyl triphenylamine -3 and 5-dicarboxylic acid chloride were obtained.

[0074] next, this 4' and 4" - dimethyl triphenylamine -3 and 5-dicarboxylic acid chloride are reacted at - 78 degrees C in dimethylformamide with a t-butoxy lithium aluminum hydride [LiAlH (O-t-C4H9)3] -- making -- 4' of the object, and 4" - dimethyl triphenylamine -3 and 5-dialdehyde were obtained.

[0075] 4' and 4' which were obtained by the approach of the vacuum evaporationo polymerization above -- ' -- the source of the 1st vacuum evaporationo and the source of the 2nd vacuum evaporationo were filled up with - dimethyl triphenylamine -3, 5-dialdehyde, and 1 of marketing and 4-phenylenediamine (Wako Pure Chem make), respectively.

[0076] After using and cleaning ultrasonically an acetone, ultrapure water, a substrate cleaning agent, ultrapure water, and isopropyl alcohol in this sequence, using 1000A glass with ITO (Hoya Corp. make) as a substrate, it pulled up from the isopropyl alcohol steam. This substrate was installed in the substrate electrode holder in which the temperature control in vacuum evaporationo equipment is possible.

[0077] It decompressed until the total pressure in equipment was set to 1x10 to 5 or less Torrs. The shutter of the source of vacuum evaporationo is closed beforehand, and resistance heating of said source of vacuum evaporationo was carried out. The temperature of each source of vacuum evaporationo was set up acting as the monitor of the vapor rate of the monomer from each source of vacuum evaporationo. Next, the shutter of the source of vacuum evaporationo was opened, and the vapor rate of 4', the 4"-dimethyl triphenylamine -3, 5-dialdehyde, and 1 and 4-phenylenediamine was controlled so that a thin film was formed at the membrane formation rate of 4A / sec. The shutter was closed in the place where the thickness of the thin film formed on the substrate showed 1000A by measurement by the quartz-resonator type thickness gage. In addition, the vapor rate of 4', the 4"-dimethyl triphenylamine -3, 5-dialdehyde, and 1 and 4-phenylenediamine was controlled to be set to 1:1 by the mole ratio.

[0078] Thus, when the front face of the produced thin film was observed with the scanning electron microscope, it excelled in surface smoothness extremely and checked that it was a thin film without a pinhole.

The thin film with a thickness of 1 micrometer was produced on the substrate by performing the same actuation as the above, using aluminum substrate with a thickness of 0.5mm as a structure check substrate of a thin film.

[0079] When FT-IR spectrum of this thin film was measured with the reflection method, the peak of 3370 and 3200cm-1 based on the N-H stretching vibration of the amino group of 1 and 4-phenylenediamine was extinguished, and the peak of 1600cm-1 based on the C=N stretching vibration of an azomethine radical was accepted. It checked from this 4' and that target polyazo methine was generating by the polymerization reaction of the 4"-dimethyl triphenylamine -3, 5-dialdehyde, and 1 and 4-phenylenediamine.

[0080] On the polyazo methine thin film produced on the fabrication of thin film electroluminescence devices, and the luminescence check aforementioned glass substrate, the AgMg electrode used as an electronic notes telegram pole was produced. The evaporation rate of Mg set up the evaporation rate of 10A/sec., and Ag so that it might become 1A / sec.

[0081] When the AgMg electrode was just made negative for the ITO electrode and direct-current 15V were impressed to the obtained thin film electroluminescence devices, the electroluminescence which has peak wavelength in 520nm arose.

[0082]

[Example 2]

2, 5-screw (p-aminophenyl) - After heating at 130 degrees C for 24 hours, mixing and stirring the synthetic p-nitrobenzoic acid and the hydrazine hydrate of 1, 3, and 5-OKISA diazole to polyphosphoric acid, it added to iced water. It filters, and the obtained settlings were often washed in order of distilled water, a sodium bicarbonate water solution, and distilled water, and were dried. It recrystallized [nitrobenzene] after that and the yellow crystal was obtained.

[0083] This crystal and Raney The catalyst was mixed, it added to dioxane and hydrogenation was performed at 55 degrees C for 10 hours. After filtering a catalyst, -5% sodium-hydroxide water solution of hydrochloric acids washes a product 5%, and they are 2 of powder, and 5-screw (p-aminophenyl). - 1, 3, and 5-OKISA diazole was obtained.

[0084] 2, 5-screw (p-aminophenyl) which were compounded by the approach of the vacuum evaporationo polymerization above - The source of the 1st vacuum evaporationo and the source of the 2nd vacuum evaporationo were filled up with the terephthal aldehyde (Wako Pure Chem make) of 1, 3, and 5-OKISA diazole and marketing, respectively.

[0085] After using and cleaning ultrasonically an acetone, ultrapure water, a substrate cleaning agent, ultrapure water, and isopropyl alcohol in this sequence, using 1000A glass with ITO (Hoya Corp. make) as a substrate, it pulled up from the isopropyl alcohol steam. This substrate was installed in the substrate electrode holder in which the temperature control in vacuum evaporationo equipment is possible.

[0086] It decompressed until the total pressure in equipment was set to 1x10 to 5 or less Torrs. The shutter of the source of vacuum evaporationo is closed beforehand, and resistance heating of said source of vacuum evaporationo was carried out. The temperature of each source of vacuum evaporationo was set up acting as the monitor of the vapor rate of the monomer from each source of vacuum evaporationo. Next, it is 2 and 5-screw (p-aminophenyl) so that the shutter of the source of vacuum evaporationo may be opened and a thin film may be formed at the membrane formation rate of 4A / sec. - The vapor rate of 1, 3, and 5-OKISA diazole and a terephthal aldehyde was controlled. The shutter was closed in the place where the thickness of the thin film formed on the substrate showed 1000A by measurement of a quartz-resonator type thickness gage. In addition, 2, 5-screw (p-aminophenyl) - The vapor rate of 1, 3, and 5-OKISA diazole and a terephthal aldehyde was controlled to be set to 1:1 by the mole ratio.

[0087] Thus, when the front face of the produced thin film was observed with the scanning electron microscope, it excelled in surface smoothness extremely and checked that it was a thin film without a pinhole.

The macromolecule thin film with a thickness of 1 micrometer was produced on the substrate by performing the same actuation as the above, using aluminum substrate with a thickness of 0.5mm as a structure check substrate of a thin film.

[0088] When FT-IR spectrum of this giant-molecule thin film was measured with the reflection method, the peak of 3350 and 3200cm-1 based on the N-H stretching vibration of the amino group of 1 and 4-phenylenediamine was extinguished, and the peak of 1600cm-1 based on the C=N stretching vibration of an azomethine radical or an OKISA thiazole ring was accepted. 2 from this, 5-screw (p-aminophenyl) - It checked that target polyazo methine was generating by the polymerization reaction of 1, 3, and 5-OKISA diazole and a terephthal aldehyde.

[0089] On the polyazo methine thin film produced on the fabrication of thin film electroluminescence devices, and the luminescence check aforementioned glass substrate, the AgMg electrode used as an electronic notes telegram pole was produced. The evaporation rate of Mg set up the evaporation rate of 10A/sec., and Ag so that it might become 1A / sec.

[0090] When the AgMg electrode was just made negative for the ITO electrode and direct-current 15V were impressed to the obtained thin film electroluminescence devices, the electroluminescence which has peak wavelength in 480nm arose.

[Translation done.]

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(54)【発明の名称】　ポリアゾメチンおよびその製造方法、ならびに薄膜電界発光素子

(57)【要約】

【構成】　下記式で表される繰り返し単位を有するポリアゾメチンおよびその製造方法。

－（Ｘ－Ｎ＝ＣＨ－Ｙ－ＣＨ＝Ｎ）－

（式中、Ｘは芳香族炭化水素基またはヘテロ環化合物から誘導される基を示し、Ｙは芳香族三級アミン骨格を有する基を示す。）

前記電界発光層、ホール注入・輸送層および電子注入・輸送層のうち少なくとも１つの層が、上記ポリアゾメチンからなる薄膜電界発光素子。

【効果】　本発明のポリアゾメチンは、電子輸送性、発光性またはホール輸送性に優れた薄膜を形成する薄膜電界発光素子材料などとして用いられる。この薄膜電界発光素子は、耐熱性および耐久性に優れている。

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【特許請求の範囲】

【請求項1】　下記式［Ｉ］で表される繰り返し単位を＊

$$-\!\!\left\langle X-N=CH-Y-CH=N \right\rangle\!\!- \quad \cdots \quad [I]$$

（式中、Xは芳香族炭化水素基またはヘテロ環化合物から誘導される基を示し、Yは芳香族三級アミン骨格を有する基を示す。）

【請求項2】　前記式［Ｉ］においてXが芳香族炭化水素基または炭素原子数４以上の窒素含有芳香族ヘテロ環化合物から誘導される基である請求項１に記載のポリア※

$$X-(NH_2)_2 \quad \cdots \quad [II]$$

（式中、Xは芳香族炭化水素基またはヘテロ環化合物か★

$$Y-(CHO)_2 \quad \cdots \quad [III]$$

（式中、Yは芳香族三級アミン骨格を有する基を示す。）

【請求項4】　少なくとも一方が透明である一対の電極間に電界発光層を有し、かつ必要に応じて前記電極の一方と前記電界発光層との間にホール注入・輸送層または電子注入・輸送層を有するか、または前記電極の一方と前記電界発光層との間にホール注入・輸送層を有すると☆

$$-\!\!\left\langle X-N=CH-Y-CH=N \right\rangle\!\!- \quad \cdots \quad [I]$$

（式中、Xは芳香族炭化水素基またはヘテロ環化合物から誘導される基を示し、Yは芳香族三級アミン骨格を有する基を示す。）

【請求項5】　前記電界発光層が、下記式［II］で表さ◆

$$X-(NH_2)_2 \quad \cdots \quad [II]$$

（式中、Xは芳香族炭化水素基またはヘテロ環化合物か＊

$$Y-(CHO)_2 \quad \cdots \quad [III]$$

（式中、Yは芳香族三級アミン骨格を有する基を示す。）

【請求項6】　前記式［Ｉ］および式［II］においてX が芳香族炭化水素基または炭素原子数４以上の窒素含有芳香族ヘテロ環化合物から誘導される基である請求項４または請求項５に記載の薄膜電界発光素子。

【発明の詳細な説明】

【０００１】

【発明の技術分野】本発明は、新規なポリアゾメチンおよびその製造方法、ならびに該ポリアゾメチンからなる層を有する薄膜電界発光素子に関し、さらに詳しくは、薄膜電界発光材料などとして用いられるポリアゾメチンおよびその製造方法、ならびにフラットパネルディスプレイあるいはそのバックライトなどとして使用される薄膜電界発光素子に関するものである。

【０００２】

【発明の技術的背景】有機薄膜電界発光素子は、完全固体素子であるため耐衝撃性に優れ、かつ自己発光のため視認性が高いという特徴を有しており、現在フラットパネル型ディスプレイとして用いる研究が活発に行われている。

【０００３】有機薄膜電界発光素子とは、特定の有機材料に対して電極から電圧を印加することにより注入され※

2

＊有することを特徴とするポリアゾメチン；

【化１】

※ゾメチン。

【請求項3】　下記式［II］で表されるジアミノ化合物と、下記式［III］で表されるジアルデヒド化合物とを反応させて請求項１に記載のポリアゾメチンを製造することを特徴とするポリアゾメチンの製造方法；

★ら誘導される基を示す。）

☆ともに、前記電極の他方と前記電界発光層との間に電子注入・輸送層を有する薄膜電界発光素子において、前記電界発光層が、下記式［Ｉ］で表される繰り返し単位を有するポリアゾメチンからなることを特徴とする薄膜電界発光素子；

【化２】

◆れるジアミノ化合物と、下記式［III］で表されるジアルデヒド化合物とを蒸着重合して得られる層である請求項４に記載の薄膜電界発光素子；

＊ら誘導される基を示す。）

※たホールと電子とが、その材料内で再結合して緩和することにより材料固有の光（蛍光）を発光する素子である。このような素子に用いられる有機材料としては、青色に電界発光をするアントラセン単結晶が古くから知られている。しかし、この単結晶は厚さが数十μm～数mmと厚いため、発光させるためには、数百Ｖの駆動電圧が必要であった。その後、薄膜化することにより駆動電圧は低減化されたが、注入効率は未だ充分ではない。

【０００４】また、有機材料を用いた積層型電界発光素子も報告されており、この積層型電界発光素子は、ＩＴＯ上にホール注入層、発光層、Ｍｇ：Ａｇの電子注入電極をこの順に蒸着積層したものであり、数十Ｖの印加電圧で発光が観測されている。しかし、蒸着した材料が結晶化して素子が発光しなくなったり、あるいは発光に伴う発熱によって電極と有機材料からなる層との間が剥離することもあった。

【０００５】このような問題を解決する手段として、有機材料を高分子化する試みがあり、電荷輸送性高分子材料に低分子化合物を添加したり、あるいはπ共役系高分子材料を用いた電界発光素子が報告されている。たとえばホール輸送材料として知られているポリ（メチルフェニルシラン）に発光性色素を微量ドープしてスピンコート薄膜とし、これに電子輸送材料を真空蒸着して作製し

た2層積層型電界発光素子や、ホール輸送材料であるポリ（N-ビニルカルバゾール）に発光性色素と電子輸送性化合物を添加してスピンコートして作製した単層型電界発光素子などが提案されている。一方、π共役系高分子材料であるポリ（フェニレンビニレン）およびその共重合体や部分変換体、ポリ（p-フェニレン）、ポリ（アルキルチオフェン）、ポリ（フルオレノン）を用いた高分子電界発光素子も報告されている。これらの高分子材料を用いることにより電界発光素子の耐久性上問題となっている発熱による薄膜の結晶化を大幅に改良できるものと期待されている。

【0006】しかしながら、高分子薄膜の作製プロセスとして溶液から薄膜を形成するウエットプロセスを採用すると、各種不純物を素子中に混入させたり表面が汚染されることがある。

【0007】また、一旦形成された有機薄膜の上にさらに有機層を塗布形成する際には、上層を塗布形成する際に使用する溶剤は、下層が溶解あるいは溶出しないものを選択しなければならないし、高分子材料や含有させる低分子材料の選択の適用範囲が制限されてくる。

【0008】そこで、ドライプロセスによる電界発光素子の作製法である蒸着重合法が提案されている。特開平5－271651号公報には、蒸着重合法による電界発光素子の作製方法が開示されている。しかしながら電界発光機能を示すための電荷輸送を担う分子であるテトラ*

*シアノキノジメタン（TCNQ）やテトラチオフルバレン（TTF）などは、その平面性が高いため、結晶化を起こしやすい傾向にある。また、側鎖に電荷輸送基を有するポリ（N-ビニルカルバゾール）では、それら分子の平面性が高いために分子間相互作用を起こして二量体化し、そのダイマー部分が電荷（ホール）輸送のトラップとなることが報告されており、側鎖に電荷輸送基を有する高分子薄膜では電荷輸送に不利な面が存在する。

【0009】したがって、電荷輸送を担う分子に要求される条件として、❶平面性が崩れている、❷電荷輸送を担う基が高分子の主鎖中に存在する、などが考えられる。これらの条件を満たすことにより高性能な有機薄膜電界発光素子が可能になると期待される。

【0010】

【発明の目的】本発明は、上記のような現状に鑑みてなされたものであって、薄膜電界発光材料として好適に用いられるポリアゾメチンおよびその製造方法を提供することを目的とするとともに、耐熱性および耐久性に優れた薄膜電界発光素子を提供することを目的としている。

【0011】

【発明の概要】本発明に係るポリアゾメチンは、下記式［I］で表される繰り返し単位を有することを特徴としている。

【0012】

【化3】

$$-(X-N=CH-Y-CH=N)- \quad \cdots [I]$$

【0013】（式中、Xは芳香族炭化水素基またはヘテロ環化合物から誘導される基を示し、Yは芳香族三級アミン骨格を有する基を示す。）

前記式［I］においてXが芳香族炭化水素基または炭素原子数4以上の窒素含有芳香族ヘテロ環化合物から誘導される基であるポリアゾメチンは、特に薄膜電界素子材料として有用である。

※【0014】本発明に係るポリアゾメチンの製造方法は、下記式［II］で表されるジアミノ化合物と、下記式［III］で表されるジアルデヒド化合物とを反応させて前記式［I］で表される繰り返し単位を有するポリアゾメチンを得ることを特徴としている。

【0015】

※

$$X-(NH_2)_2 \quad \cdots [II]$$

（式中、Xは芳香族炭化水素基またはヘテロ環化合物か★ら誘導される基を示す。）

★

$$Y-(CHO)_2 \quad \cdots [III]$$

（式中、Yは芳香族三級アミン骨格を有する基を示す。）

本発明に係る薄膜電界発光素子は、少なくとも一方が透明である一対の電極間に電界発光層を有し、かつ必要に応じて前記電極の一方と前記電界発光層との間にホール注入・輸送層または電子注入・輸送層を有するか、または前記電極の一方と前記電界発光層との間にホール注入・輸送層を有するとともに、前記電極の他方と前記電界発光層との間に電子注入・輸送層を有する薄膜電界発光素子において、前記電界発光層、ホール注入・輸送層および電子注入・輸送層のうち少なくとも一つの層が、上記ポリアゾメチンからなることを特徴としている。

【0016】本発明では、前記電界発光層が、前記式［II］で表されるジアミノ化合物と、前記式［III］で☆表されるジアルデヒド化合物とを蒸着重合して得られる層であることが好ましい。

【0017】本発明では、前記ポリアゾメチンからなる層が、前記式［II］で表されるジアミノ化合物と、前記式［III］で表されるジアルデヒド化合物とを蒸着重合して得られる層であることが好ましい。

【0018】

【発明の具体的説明】以下、本発明に係るポリアゾメチンおよびその製造方法、ならびに薄膜電界発光素子について具体的に説明する。

【0019】本発明のポリアゾメチンは、下記式［I］で表される繰り返し単位を有する高分子化合物である。

【0020】

【化4】

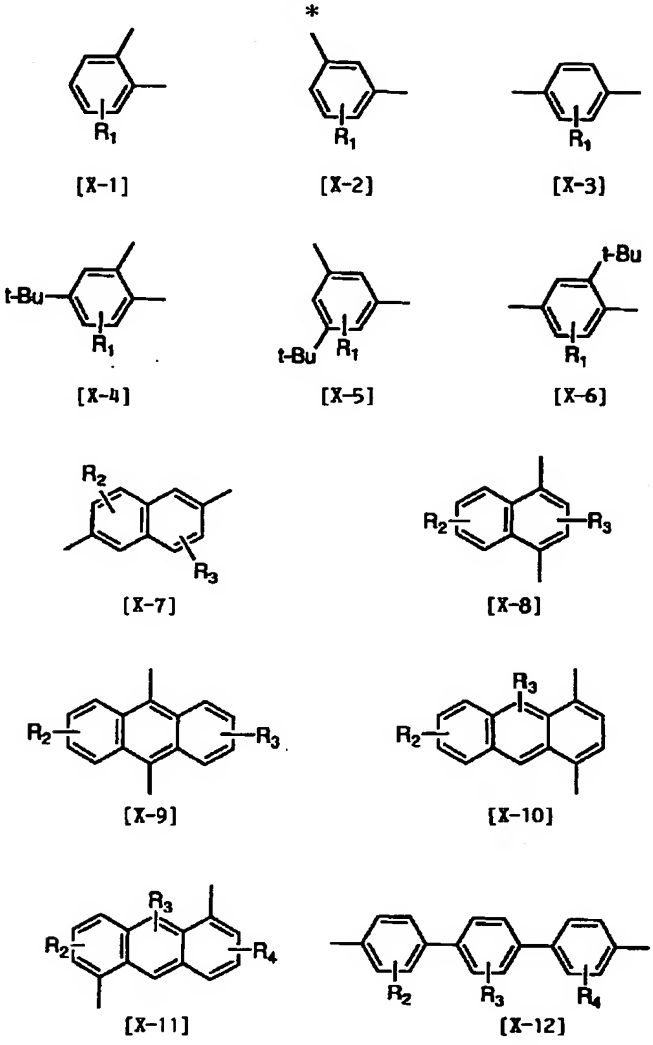
5　　6

$$-(-X-N=CH-Y-CH=N-)- \quad \cdots \quad [1]$$

【0021】式中、Xは芳香族炭化水素基またはヘテロ環化合物から誘導される基を示し、具体的には、下記のような基が挙げられる。

＊【0022】

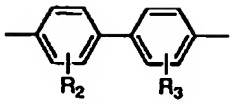
【化5】



【0023】

※　※【化6】

7　　8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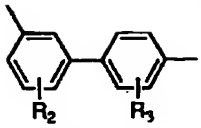
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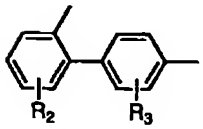
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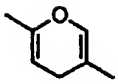
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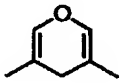
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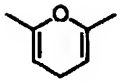
[X-18]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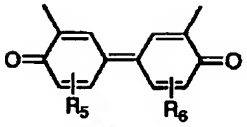
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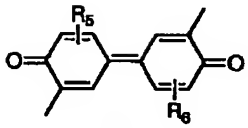
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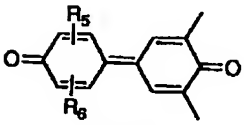
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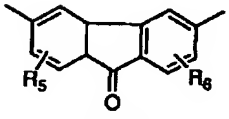
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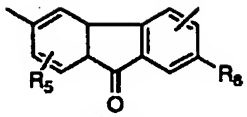
【0024】　　＊30＊【化7】

9　　10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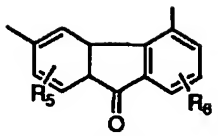
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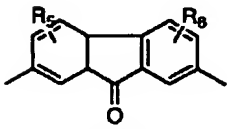
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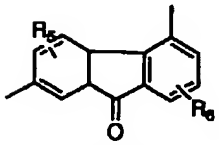
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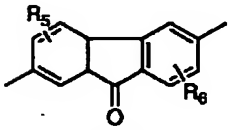
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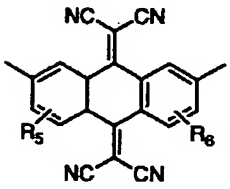
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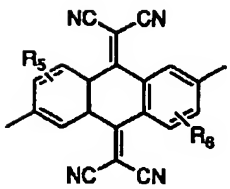
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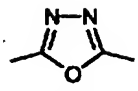
【0025】　　＊　＊【化8】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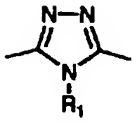
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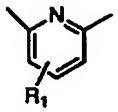
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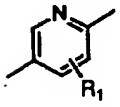
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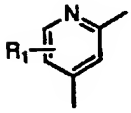
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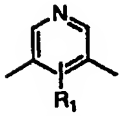
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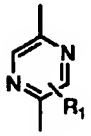
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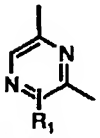
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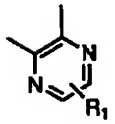
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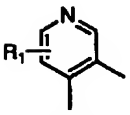
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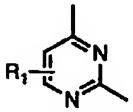
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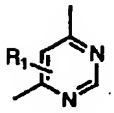
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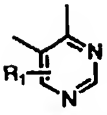
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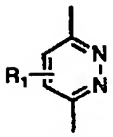
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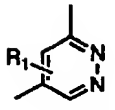
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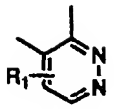
【0026】　　＊30＊【化9】



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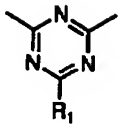

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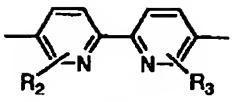

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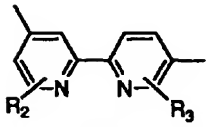

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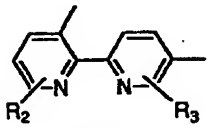

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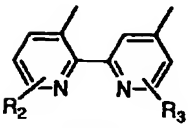

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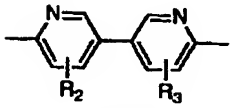

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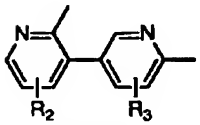

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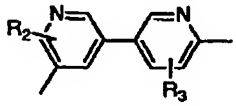

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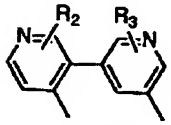

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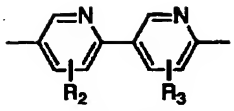
【0027】　　＊　＊【化10】

15　　16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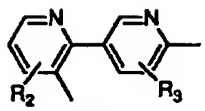
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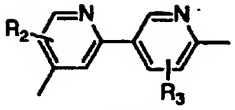
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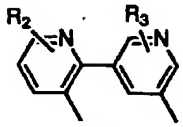
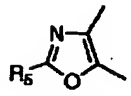
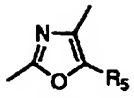

[X-59]


[X-60]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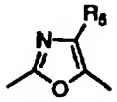
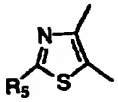

[X-62]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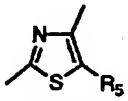
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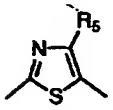
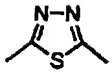

[X-65]

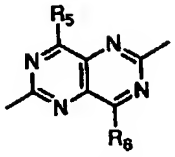

[X-66]


[X-67]


[X-68]


[X-69]

【0028】　　＊30＊【化11】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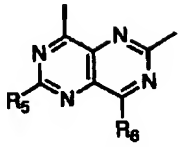
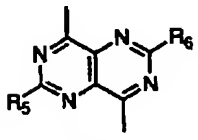

[X-71]


[X-72]

【0029】なお、上記式中R^1～R^6は、それぞれ独立して水素原子、メチル、エチル、プロピル、ブチルなどの炭素原子数1～10のアルキル基、ベンジル、フェネチルなどの炭素原子数7～10アラルキル基、メトキシ、エトキシ、プロポキシ、ブトキシなどの炭素原子数1～10のアルキルオキシ基を示す。

【0030】上記したXで示される基の中では、芳香族炭化水素基または炭素原子数4以上の芳香族ヘテロ環化※50

※合物から誘導される基が好ましく、炭素原子数4以上の窒素含有芳香族ヘテロ環化合物から誘導される基がより好ましい。

【0031】窒素原子の電気陰性度は炭素原子の電気陰性度より大きいので、電子輸送に必要な電子受容性を向上させることができる。したがって式［I］におけるXとして窒素含有ヘテロ環化合物から誘導される基を用いることにより、電子注入・輸送性を付与することができ

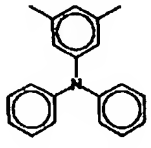
る。

【0032】Yは、電子写真感光体などで知られている各種化合物の誘導体残基、たとえば特開昭63－295695号公報に開示されているような芳香族三級アミンあるいはポルフィリン化合物、特開昭53－27033号公報、特開昭54－58445号公報、特開昭54－149634号公報、特開昭54－64299号公報、特開昭55－144250号公報、特開昭56－119132号公報、特開昭61－295558号公報、特開＊昭61－98303号公報などに開示されている化合物から誘導される基が挙げられる。このような基は、ホール注入・輸送性を付与する。

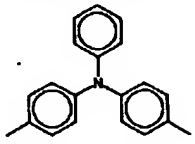
【0033】本発明ではYは、芳香族三級アミン骨格を有する基であることが好ましく、具体的には、下記のような基が挙げられる。

【0034】

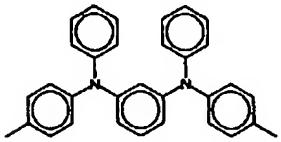
【化12】



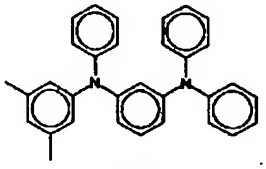
[Y-1]



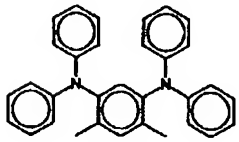
[Y-2]



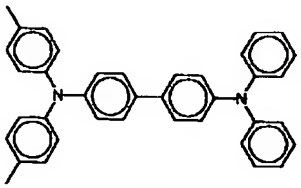
[Y-3]



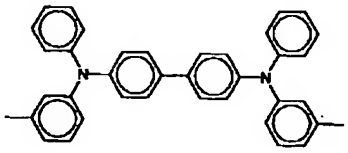
[Y-4]



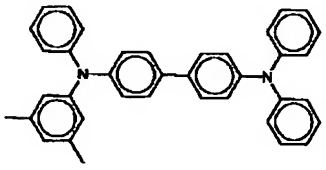
[Y-5]



[Y-6]

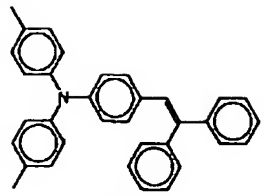


[Y-7]

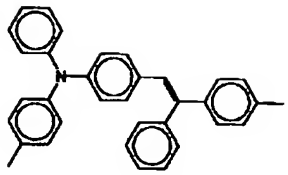


[Y-8]

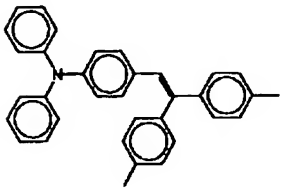
【0035】　　※　※【化13】



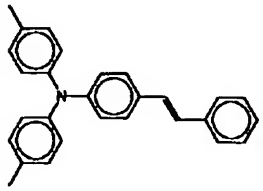
[Y-9]



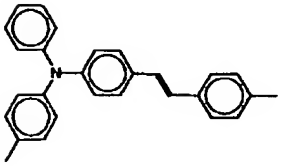
[Y-10]



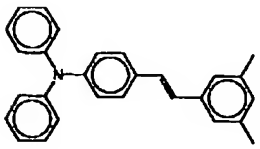
[Y-11]



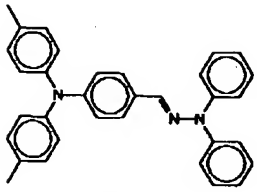
[Y-12]



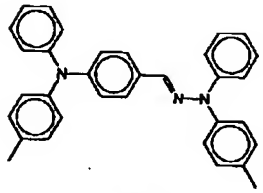
[Y-13]



[Y-14]

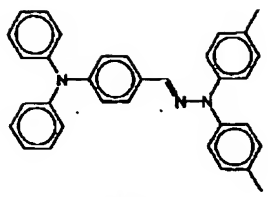


[Y-15]

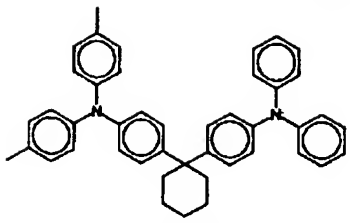


[Y-16]

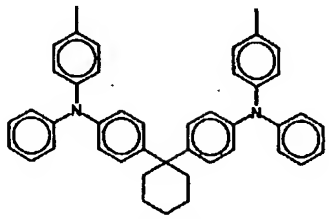
【0036】　　＊30＊【化14】



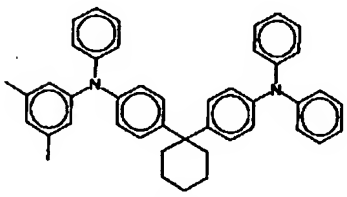
[Y-17]



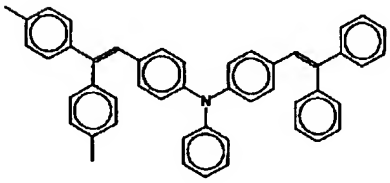
[Y-18]



[Y-19]

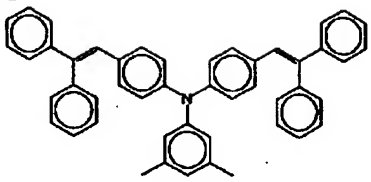


[Y-20]

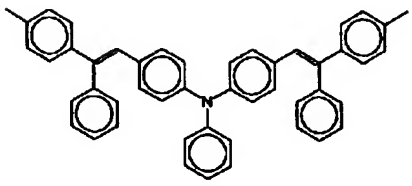


[Y-21]

【0037】
【化15】



[Y-22]



[Y-23]

【0038】上記ような芳香族三級アミン骨格を有する基は、窒素原子の不対電子により平面性が崩れた構造（ピラミッド型）を有する。このような平面性が崩れた構造を有する分子は、分子間相互作用を起こしにくいため電荷輸送のトラップとなることがなく電荷輸送には好都合である。

【0039】本発明に係るポリアゾメチンはその重合度が、2以上、好ましくは5以上、より好ましくは10以上である。前記式［I］で表されるアゾメチン繰り返し単位を有するポリマーは、ジメチルホルムアミド（DMF）、ジメチルスルホオキサイド（DMSO）などの極性溶媒に溶解する場合は、粘度法によりその重合度を求めることができる。

【0040】本発明に係るポリアゾメチンは、たとえば薄膜電界発光素子材料として用いることができる。この場合ポリアゾメチンは、X，Yで示される基を適宜選択することにより、電界発光層、電子注入・輸送層またはホール注入・輸送層とすることができる。

【0041】本発明のポリアゾメチンは、電界発光機能、電荷注入・輸送機能を有する基が主鎖に組み込まれており、結晶化しにくく、耐熱性および耐久性に優れている。本発明のポリアゾメチンは、下記式［II］で表されるジアミノ化合物と、下記式［III］で表されるジアルデヒド化合物とを反応させることにより製造すること

ができる。

$X-(NH_2)_2$　　… [II]

（式中、Xは前記式［Ｉ］におけるXと同様である。）

$Y-(CHO)_2$　　… [III]

（式中、Yは前記式［Ｉ］におけるYと同様である。）

本発明のポリアゾメチンを薄膜電界発光素子材料として使用する場合は、上記式［II］で表されるジアミノ化合物と、上記式［III］で表されるジアルデヒド化合物とを蒸着重合させ、基板上にポリアゾメチンを薄膜として形成する。蒸着重合によるポリアゾメチン薄膜の製膜法は、公知の各種方法により行うことができる。

【００４３】より具体的には、後述するように上記式［II］で表されるジアミノ化合物と、上記式［III］で表されるジアルデヒド化合物をそれぞれ蒸着源とし、真空槽内で２元蒸着を行い、基板上でモノマーを反応させることによりポリアゾメチン薄膜を得る。

【００４４】このような方法によると、不純物の混入が少なく、ピンホールもなく、耐久性に優れた薄膜を形成することができる。次に、本発明に係る薄膜電界発光素子について説明する。

【００４５】図１～４は、本発明に係る薄膜電界発光素子の構成を模式的に示す断面図であり、図中１は負極を示し、２は正極を示し、３は電界発光層を示し、４は電子注入・輸送層を示し、５はホール注入・輸送層を示す。図５は、本発明に係る薄膜電界発光素子の製造に用いられる真空蒸着装置の一例を示す概略図である。

【００４６】本発明に係る薄膜電界発光素子１０は、たとえば図１に示すように一対の電極（負極１および正極※２）間に電界発光層３を有する積層体である。負極１としては、電界発光層３への電子の注入効率が高く、しかも電界発光層３に電子を繰り返し注入できる電極、たとえばＭｇ、Ｉｎ、Ｃａ、Ａｌおよびこれらの合金などの公知の電極が使用できる。

【００４７】正極２としては、電界発光層３へのホール（正孔）の注入効率が高く、しかも電界発光層３にホールを繰り返し注入できる電極、たとえばインジウムスズオキサイド（ＩＴＯ）、酸化スズ（ＮＥＳＡ）、Ａｕ、Ｐｔ、Ａｇなどの公知の電極単体およびＩＴＯあるいはＮＥＳＡなどの透明電極上にＡｕ、Ｐｔ、Ａｇなどを半透明に積層した電極などが使用できる。

【００４８】前記負極１および正極２のいずれか一方は透明であり、この透明電極を通して電界発光層３からの光が照射できるようになっている。また、負極１および正極２のいずれか一方は、通常ガラスやポリマーフィルムなどの透明基板上に形成されている。たとえば、正極２として、ガラスやポリマーフィルム上に薄膜状に形成されたＩＴＯ電極が用いられる。

【００４９】電界発光層３は、下記式［Ｉ］で表される繰り返し単位を有するポリアゾメチンから形成されている。

【００５０】

【化１６】

$$+X-N=CH-Y-CH=N+ \quad \cdots [I]$$

【００５１】（式中、XおよびYは前記と同様である。）

XおよびYは、負極１、正極２を形成する材料の種類、および電界発光層３から発光される光の波長などに応じて適宜選択される。

【００５２】本発明に係る薄膜電界発光素子１０は、図２に示すように負極１と電界発光層３との間に電子注入・輸送層４を有していてもよく、図３に示すように正極２と電界発光層３との間にホール注入・輸送層５を有していてもよく、また図４に示すように負極１と電界発光層３との間に電子注入・輸送層４を有し、かつ正極２と電界発光層３との間にホール注入・輸送層５を有していてもよい。

【００５３】ここで電子注入・輸送層４は、負極１から電界発光層３に注入される電子の注入効率を高める役割を果たし、ホール注入・輸送層５は、正極２から電界発光層３に注入されるホールの注入効率を高める役割を果たす。

【００５４】薄膜電界発光素子１０が、電子注入・輸送層４および／またはホール注入・輸送層５を有する場合、電界発光層３、電子注入・輸送層４および／または★ホール注入・輸送層５のいずれか一つの層が前記式［Ｉ］で表される繰り返し単位を有するポリアゾメチンから形成されている。前記ポリアゾメチンから形成される層以外の層は公知の材料で形成されている。

【００５５】本発明では、薄膜電界発光素子１０が、電子注入・輸送層４および／またはホール注入・輸送層５を有する場合、電界発光層３、電子注入・輸送層４、ホール注入・輸送層５のすべてが前記ポリアゾメチンから形成されていることが望ましい。この場合、電界発光層３は電界発光性に優れたポリアゾメチンで形成され、電子注入・輸送層４は電子注入・輸送性に優れたポリアゾメチンで形成され、ホール注入・輸送層５はホール注入・輸送性に優れたポリアゾメチンで形成される。なお、電界発光層３を形成するポリアゾメチンの前記式［Ｉ］におけるXおよびYのうち少なくとも一方は、ホール注入・輸送層５を形成するポリアゾメチンの前記式［Ｉ］におけるXまたはYとは異なっており、電界発光層３を形成するポリアゾメチンの前記式［Ｉ］におけるXおよびYのうち少なくとも一方は、電子注入・輸送層４を形成するポリアゾメチンの前記式［Ｉ］におけるXまたはYとは異なっており、電子注入・輸送層４を形成するポ

リアゾメチンの前記式［Ｉ］におけるＸおよびＹのうち少なくとも一方は、ホール注入・輸送層５を形成するポリアゾメチンの前記式［Ｉ］におけるＸまたはＹとは異なっている。

【００５６】電界発光層３を形成するポリアゾメチンの前記式［Ｉ］におけるＸおよびＹは、電界発光層３から発光される光の波長などに応じて適宜選択され、電子注入・輸送層４を形成するポリアゾメチンの前記式［Ｉ］におけるＸおよびＹは、負極１を形成する材料の種類などに応じて適宜選択され、ホール注入・輸送層５を形成するポリアゾメチンの前記式［Ｉ］におけるＸおよびＹは、正極２を形成する材料の種類などに応じて適宜選択される。

【００５７】電界発光層３、電子注入・輸送層４およびホール注入・輸送層５は、たとえば蒸着重合法により形成することができる。このような薄膜電界発光素子１０を形成する電界発光層３の厚さは、通常１００～２０００Å、好ましくは２００～１２００Åであり、電子注入・輸送層４の厚さは、通常５０～２０００Å、好ましくは５０～５００Åであり、ホール注入・輸送層５の厚さは、通常５０～２０００Å、好ましくは５０～５００Åである。

【００５８】本発明では、薄膜電界発光素子１０の負極１または正極２上に酸化防止膜などの保護膜を有していてもよい。このような保護膜の存在によって電極の安定性が増し、素子としての実用性・耐久性が向上する。保護膜は、スピンコート法あるいは蒸着法などの方法により形成することができる。このような保護膜としては、たとえば金属、金属酸化物、金属フッ化物などの封止剤を用いることができる。

【００５９】本発明の薄膜電界発光素子は、電界発光層、電子注入・輸送層およびホール注入・輸送層のうち少なくとも一つの層が前記式［Ｉ］で表される繰り返し単位を有するポリアゾメチンから形成されているので結晶化による劣化や、電極などからの剥離を起こしにくい。また、ドライプロセスにより形成されたポリアゾメチンからなる層は、不純物の混入が少なく、ピンホールがない。

【００６０】このような本発明の薄膜電界発光素子１０は、負極１および正極２から電圧を印加することによって発光させることができる。印加する電圧はＤＣ電圧のみならず、パルス印加や三角波などの駆動波形によって発光させることも可能である。特にパルスを用いた場合には、ＤＣ電圧に比べて消費電力が格段に少なくなるだけでなく、素子の寿命の向上にもつながる。このように特定の電圧の波形で駆動することにより、薄膜電界発光素子を表示素子として利用することもできる。

＊【００６１】また、本発明の薄膜電界発光素子は、電子注入電極およびホール注入電極としてマトリックス電極あるいは薄膜トランジスタ（ＴＦＴ）電極等のパターンを施して駆動し、液晶と一体化させたバックライトや表示素子として利用することも可能である。

【００６２】このような薄膜電界発光素子は、通常、下記（ｉ）～（vi）の工程を経て製造される。

（ｉ）基板上に第１の電極を形成する工程

（ii）第１の電極上に所望により第１の電荷注入・輸送層を形成する工程

（iii）第１の電極上、または前記工程（ii）で第１の電荷注入・輸送層を形成した場合は第１の電荷注入・輸送層上に電界発光層（３）を形成する工程

（iv）電界発光層（３）上に所望により第１の電荷注入・輸送層とは反対符号の電荷を注入・輸送する能力を有する第２の電荷注入・輸送層を形成する工程〔たとえば、第１の電荷注入・輸送層が電子注入・輸送層（４）である場合、第２の電荷注入・輸送層はホール注入・輸送層（５）である〕

（ｖ）電界発光層（３）上、または前記工程（iv）で第２の電荷注入・輸送層を形成した場合は第２の電荷注入・輸送層上に対向電極を形成する工程〔たとえば、工程（ｉ）で形成された電極が負極（１）である場合、対向電極は正極（２）である〕

（vi）所望により対向電極上に電界発光素子の封止層を形成する工程

本発明では、薄膜電界発光素子を製造する際には、基板上に電極を成形する工程から対向電極を形成する工程までの全工程〔前記工程（ｉ）から工程（ｖ）〕を同一チャンバー内で連続的に行い、かつ対向電極を形成する工程に到るまでの間、チャンバー内に外気を流入させることなく次工程を行うことが好ましい。

【００６３】このようにして薄膜電界発光素子を製造すると、外気中に含まれる埃が形成した薄膜に付着したり、薄膜が外気中の酸素あるいは水分を吸着して劣化することがない。

【００６４】本発明の薄膜電界発光素子では、電界発光層（３）、第１および第２の電荷注入・輸送層〔電子注入・輸送層（４）およびホール注入・輸送層（５）〕のうち少なくとも１つの層は、前記式［Ｉ］で表されるポリアゾメチンからなり、このポリアゾメチンからなる層は、蒸着重合法により形成される。

【００６５】蒸着重合により前記層を形成する際には、下記式［II］で表されるジアミノ化合物と、下記式［III］で表されるジアルデヒド化合物とが重合用モノマーとして用いられる。

【００６６】

… ［II］

… ［III］

$X-(NH_2)_2$

（式中、Ｘは前記式［Ｉ］におけるＸと同様である。）

$Y-(CHO)_2$

（式中、Yは前記式［Ｉ］におけるＹと同様である。）
本発明に係る薄膜電界発光素子を形成するポリアゾメチン薄膜は、たとえば、図5に示すような蒸着装置２０を用いて下記のようにして形成される。
【００６７】すなわち、
（ａ）まず真空蒸着装置２０の蒸着用チャンバー２１内に、被蒸着基板２２をセットする。（たとえば、被蒸着基板としてＩＴＯ電極付基板を用いる場合ＩＴＯ電極上に蒸着膜が形成されるようにセットする）
（ｂ）前記重合用モノマー（ジアミノ化合物［II］およびジアルデヒド化合物［III］）を、真空蒸着装置２０内の蒸着源２３ａ，２３ｂにそれぞれ載置する。
（ｃ）蒸着用チャンバー２１内の圧力が、10^{-2}Ｐａ以下、好ましくは10^{-3}Ｐａ以下になるまで蒸着用チャンバー２１内を減圧する。また、蒸着用チャンバー２１内が所定の圧力に達するまでの間に、被蒸着基板２２の被蒸着面の温度を－５０～２００℃、好ましくは２０～１００℃に調整する。
（ｄ）蒸着用チャンバー２１内が所定の圧力に達した後、この圧力下でジアミノ化合物［II］およびジアルデヒド化合物［III］が、１：１～１：３０、好ましくは１：１～１：２０のモル比で蒸発し、かつ０．１～１０Å／秒、好ましくは１～５Å／秒の蒸着速度で蒸着被膜が形成されるように蒸着源２３ａ，２３ｂの温度を制御する。この際の温度は、通常－１０～５００℃、好ましくは４０～４００℃、より好ましくは７０～３００℃、特に好ましくは１００～２５０℃である。
【００６８】上記のようにして蒸着薄膜を所望の膜厚に形成する。ポリアゾメチンからなる層を複数形成する場合は、重合用モノマーを替えて、上記の工程を繰り返す。
【００６９】
【発明の効果】本発明に係るポリアゾメチンは、電子輸送性、発光性またはホール輸送性に優れた薄膜を形成する薄膜電界発光素子材料などとして用いられる。
【００７０】本発明の薄膜電界発光素子は、耐熱性および耐久性に優れている。このような薄膜電界発光素子は、フラットパネルディスプレイまたはそのバックライトなどとして用いることができる。
【００７１】
【実施例】以下、実施例に基づいて本発明をさらに具体的に説明するが、本発明はこれら実施例に限定されるものではない。
【００７２】
【実施例１】
4',4''-ジメチルトリフェニルアミン-3,5-ジアルデヒドの合成
5-アミノイソフタル酸と$NaNO_2$／ＫＩとをＨＣｌの存在下で反応させ、5-ヨードイソフタル酸を得た。次に5-ヨードイソフタル酸とエタノールとH_2SO_4の存在下で反応させて5-ヨードイソフタル酸のエチルエステルを得た。次にこのエステルとジトリルアミンとをウルマン（Ullmann）反応させることにより4',4''-ジメチルトリフェニルアミン-3,5-ジエチルエステルを得た。
【００７３】続いて、この4',4''-ジメチルトリフェニルアミン-3,5-ジエチルエステルを水酸化ナトリウム水溶液で処理することにより4',4''-ジメチルトリフェニルアミン-3,5-ジカルボン酸を得た。さらに、この4',4''-ジメチルトリフェニルアミン-3,5-ジカルボン酸を$SOCl_2$とを反応させることにより4',4''-ジメチルトリフェニルアミン-3,5-ジカルボン酸クロライドを得た。
【００７４】次に、この4',4''-ジメチルトリフェニルアミン-3,5-ジカルボン酸クロライドをジメチルホルムアミド中で－７８℃にてt-ブトキシ水素化アルミニウムリチウム〔$LiAlH(O\text{-}t\text{-}C_4H_9)_3$〕と反応させ、目的の4',4''-ジメチルトリフェニルアミン-3,5-ジアルデヒドを得た。
【００７５】蒸着重合
前記の方法で得た4',4''-ジメチルトリフェニルアミン-3,5-ジアルデヒドと、市販の1,4-フェニレンジアミン（和光純薬製）をそれぞれ第１蒸着源および第２蒸着源に充填した。
【００７６】基板としては、１０００ÅのＩＴＯ付ガラス（ＨＯＹＡ社製）を用い、アセトン、超純水、基板洗浄剤、超純水、イソプロピルアルコールをこの順序で用いて超音波洗浄した後、イソプロピルアルコール蒸気から引き上げた。この基板を蒸着装置内の温度制御可能な基板ホルダーに設置した。
【００７７】装置内の全圧が1×10^{-5}Ｔｏｒｒ以下になるまで減圧した。予め蒸着源のシャッターを閉じておいて前記蒸着源を抵抗加熱した。各蒸着源からのモノマーの蒸発速度をモニターしながら、それぞれの蒸着源の温度を設定した。次に、蒸着源のシャッターを開いて、４Å／sec.の成膜速度で薄膜が形成されるように4',4''-ジメチルトリフェニルアミン-3,5-ジアルデヒドと1,4-フェニレンジアミンの蒸発速度を制御した。基板上に形成された薄膜の膜厚が水晶振動子式膜厚計による測定で１０００Åを示したところでシャッターを閉じた。なお、4',4''-ジメチルトリフェニルアミン-3,5-ジアルデヒドと1,4-フェニレンジアミンの蒸発速度は、モル比で１：１となるように制御した。
【００７８】このように作製した薄膜の表面を走査型電子顕微鏡で観察したところ、極めて平坦性に優れ、ピンホールのない薄膜であることを確認した。
薄膜の構造確認
基板として厚さ０．５ｍｍのＡｌ基板を用い、上記と同様の操作を行うことにより基板上に厚さ１μｍの薄膜を作製した。
【００７９】この薄膜のＦＴ－ＩＲスペクトルを反射法

で測定したところ、1,4-フェニレンジアミンのアミノ基のN－H伸縮振動に基づく３３７０，３２００cm^{-1}のピークが消滅し、アゾメチン基のC＝N伸縮振動に基づく１６００cm^{-1}のピークが認められた。このことから4',4''-ジメチルトリフェニルアミン-3,5-ジアルデヒドと1,4-フェニレンジアミンの重合反応により目的のポリアゾメチンが生成していることを確認した。

【００８０】薄膜電界発光素子の製作および発光確認

前記ガラス基板上に作製したポリアゾメチン薄膜上に、電子注入電極となるＡｇＭｇ電極を作製した。Ｍｇの蒸着速度は１０Å／sec.、Ａｇの蒸着速度は１Å／sec.となるように設定した。

【００８１】得られた薄膜電界発光素子に対して、ＩＴＯ電極を正に、ＡｇＭｇ電極を負にして直流１５Ｖを印加したところ、５２０ｎｍにピーク波長をもつ電界発光が生じた。

【００８２】

【実施例２】

2,5-ビス（p-アミノフェニル）-1,3,5-オキサジアゾールの合成

p-ニトロ安息香酸とヒドラジン水和物とをポリリン酸に混合し、撹拌しながら１３０℃で２４時間加熱した後、氷水に添加した。得られた沈澱物を沪過し、蒸留水、重炭酸ナトリウム水溶液、蒸留水の順でよく洗浄し、乾燥させた。その後ニトロベンゼンから再結晶し、黄色結晶を得た。

【００８３】この結晶とRaney 触媒とを混合してジオキサンに添加し、５５℃で１０時間水添を行った。触媒を沪過した後、生成物を５%塩酸－５%水酸化ナトリウム水溶液で洗浄し、粉末の2,5-ビス（p-アミノフェニル）-1,3,5-オキサジアゾールを得た。

【００８４】蒸着重合

上記の方法で合成した2,5-ビス（p-アミノフェニル）-1,3,5-オキサジアゾールと市販のテレフタルアルデヒド（和光純薬製）をそれぞれ第１蒸着源および第２蒸着源に充填した。

【００８５】基板としては、１０００ÅのＩＴＯ付ガラス（ＨＯＹＡ社製）を用い、アセトン、超純水、基板洗浄剤、超純水、イソプロピルアルコールをこの順序で用いて超音波洗浄した後、イソプロピルアルコール蒸気から引き上げた。この基板を蒸着装置内の温度制御可能な基板ホルダーに設置した。

【００８６】装置内の全圧が1×10^{-5}Ｔｏｒｒ以下になるまで減圧した。予め蒸着源のシャッターを閉じておいて前記蒸着源を抵抗加熱した。各蒸着源からのモノマーの蒸発速度をモニターしながら、それぞれの蒸着源の温度を設定した。次に、蒸着源のシャッターを開いて、４Å／sec.の成膜速度で薄膜が形成されるように2,5-ビス（p-アミノフェニル）-1,3,5-オキサジアゾールとテレフタルアルデヒドの蒸発速度を制御した。基板上に形

成された薄膜の膜厚が水晶振動子式膜厚計の測定により１０００Åを示したところでシャッターを閉じた。なお、2,5-ビス（p-アミノフェニル）-1,3,5-オキサジアゾールとテレフタルアルデヒドの蒸発速度は、モル比で１：１となるように制御した。

【００８７】このように作製した薄膜の表面を走査型電子顕微鏡で観察したところ、極めて平坦性に優れ、ピンホールのない薄膜であることを確認した。

薄膜の構造確認

基板として厚さ０．５ｍｍのＡｌ基板を用い、上記と同様の操作を行うことにより基板上に厚さ１μｍの高分子薄膜を作製した。

【００８８】この高分子薄膜のＦＴ－ＩＲスペクトルを反射法で測定したところ、1,4-フェニレンジアミンのアミノ基のN－H伸縮振動に基づく３３５０，３２００cm^{-1}のピークが消滅し、アゾメチン基あるいはオキサチアゾール環のC＝N伸縮振動に基づく１６００cm^{-1}のピークが認められた。このことから2,5-ビス（p-アミノフェニル）-1,3,5-オキサジアゾールとテレフタルアルデヒドの重合反応により目的のポリアゾメチンが生成していることを確認した。

【００８９】薄膜電界発光素子の製作および発光確認

前記ガラス基板上に作製したポリアゾメチン薄膜上に、電子注入電極となるＡｇＭｇ電極を作製した。Ｍｇの蒸着速度は１０Å／sec.、Ａｇの蒸着速度は１Å／sec.となるように設定した。

【００９０】得られた薄膜電界発光素子に対して、ＩＴＯ電極を正に、ＡｇＭｇ電極を負にして直流１５Ｖを印加したところ、４８０ｎｍにピーク波長をもつ電界発光が生じた。

【図面の簡単な説明】

【図１】　本発明に係る薄膜電界発光素子の構成の一例を模式的に示す断面図である。

【図２】　本発明に係る薄膜電界発光素子の構成の他の例を模式的に示す断面図である。

【図３】　本発明に係る薄膜電界発光素子の構成の他の例を模式的に示す断面図である。

【図４】　本発明に係る薄膜電界発光素子の構成の他の例を模式的に示す断面図である。

【図５】　本発明に係る薄膜電界発光素子の製造に用いられる真空蒸着装置の概略図である。

【符号の説明】

10　…　薄膜電界発光素子
1　…　負極
2　…　正極
3　…　電界発光層
4　…　電子注入・輸送層
5　…　ホール注入・輸送層
20　…　真空蒸着装置
21　…　蒸着用チャンバー

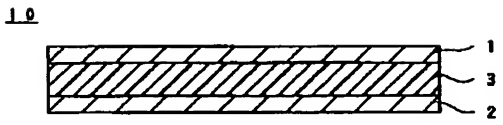
31

22　…　被蒸着基板

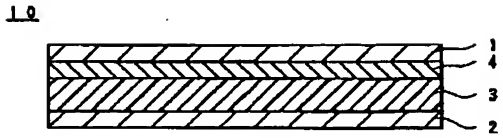
32

23a, 23b　…　蒸着源

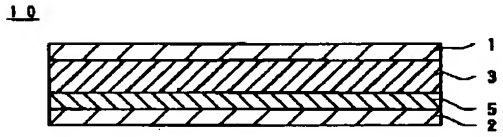
【図1】



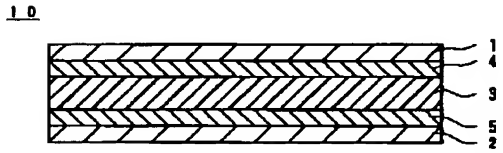
【図2】



【図3】



【図4】



【図5】